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The microstructure of metals is studied by a range of electron optical methods, grazing incidence x-ray diffraction, and conversion electron Mossbauer spectroscopy. The microstructure is related to mechanisms of plastic deformation, defect formation by ion implantation. Dynamic ion beam mixing reactions are being undertaken and studies of surface treatments and modification of surface properties. Superalloys, various alloys involving Cu, Al, Fe, Cr, Ni, Ti are being investigated as well as various precipitates in metals. Keywords;

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REVIEW OF METAL PHYSICS AT THE UNIVERSITE DE POITIERS, FRANCE

1 INTRODUCTION

The Laboratoire de Métallurgie Physique (LMP) of the University of Poitiers in France is part of the Physics Department and has built up a well-deserved reputation for excellent work in the field of microstructures of materials and their physical properties. This can be seen from the wide range of publications from this laboratory. During the period 1984 to 1986, LMP people have published over 100 articles, some 20 theses were awarded, and several patents taken out. I reported briefly on their work in *ESN* 40-11/12:428-429 (1986). A total of about 40 people are attached to the laboratory, either university faculty or persons financed by the Centre National de la Recherche Scientifique (CNRS). The laboratory is conducting many contract research projects for French companies such as SNECMA, UNIREC, Electricité de France EdF, Péchiney, Thompson CSF, and the government agency ONERA.

The research studies at Poitiers concern the microstructure of metals and ceramics in relation to:

- Mechanisms of plastic deformation in solids
- Defect formation by ion implantation, ion beam mixing, and amorphization
- Formation of precipitates (ppt) in solids
- Surface treatments and modification of surface properties.

LMP has a wide range of electron optical equipment: 100 keV and 250 keV transmission electron microscopy (TEM), scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), and photo-electron spectroscopy for chemical analysis (ESCA). This is because electron optical techniques, in particular, are fully exploited in LMP's studies of defects, ppt, dislocation systems, and subgrain boundaries. They also use a full range of x-ray diffraction equipment in conjunction with TEM.

Recent developments in equipment at Poitier include:

- An implantor for use at low temperatures (4 K to 300 K). (An earlier system permits irradiations at liquid N temperatures only.)
- Deposition by CVD or from multievaporators assisted by ion bombardment at low temperatures. This permits dynamic ion beam mixing reactions.
- Grazing incidence x-ray diffraction system to study thin surface layers. This has been constructed by modifying a low-angle x-ray scattering device. The system is known as anomalous small-angle x-ray scattering (ASAXS) (Goudeau et al., 1985).
- Conversion electron Mössbauer spectroscopy (CEMS) suitable for surface studies (Eymery et al., 1985; Bodin, 1986).
- Wear tester, sensitive at very low loads (20 g).

2 MECHANISMS OF PLASTIC DEFORMATION

The mechanisms of plastic deformation in metals have been studied in single crystals of Cu-Al alloys, relating stacking fault energy to twinning. The dislocation systems have been observed by TEM for Cu-Al (7.3 atomic percent) and Cu-Al (13.7 atomic percent) after different degrees of prestressing. Several theoretical calculations have been carried out to simulate the experimental observations of dislocation behavior (Grilhé et al., 1985).

The LMP workers have studied the microstructure of alloys having the structure type $L1_2$ found in the superalloys as phase γ. The structure type $L1_2$ is of interest due to its anomalous elastic limit at high temperatures (700°C for Ni_3Al). The studies were undertaken to understand the obstruction to dislocation movement of the $L1_2$ structure type. They have carried out TEM observations of the behavior of dislocation systems in alloys such as Ni_3Al, Ni_3Ge. The systems $Ni_{3-x}Al_{1+x}$, $Ni_{3-x}Si_{1+x}$, $Cu_{1-x}Zn_{1+x}$ are under investigation (Veyssiere et al., 1985).

The plastic deformation of the Fe-Cr-Ni alloys under cylic conditions has been studied. These are b.c.c., and the purpose of the study was to compare dislocation structures in b.c.c. with those of fcc metals (Lepinoux and Kubin, 1985). The Portevin-Le Chatelier (stick-slip) effect has been studied by TEM in Al 5-percent Mg alloys, and a model has been proposed to explain this effect (Kubin et al., 1986).

The laboratory has several ongoing studies of the effects of irradiation on metal properties. The plasticity of single crystals of Cu are known to be modified by the implantation of Cu, Al or Ar. The mechanical properties of industrial Al alloys can be modified by ion implantation. The wear resistance of the alloy NiTi is markedly improved by implanting N at 160 keV and a fluence of 10^{17} ions/cm^2. TEM and x-ray studies have been carried out to observe the microstructure of the implanted materials to understand these improvements and changes in properties (Metari et al., 1986; Kim et al., 1986; Eymery et al., 1985).

3 COVALENT STRUCTURES

The deformation mechanisms of crystals of the semiconductors Si, GaAs, $Cd_xHg_{1-x}Te$, AlN are under investigation. The dislocation structures of intrinsic Si between 300 and 700°C have been examined by TEM and also the role of oxidation in the deformation of Si at high temperatures (Grosbras et al., 1984a).

Single crystals of GaAs have been sheared in a range of crystal orientations at temperatures up to 500°C to permit TEM studies of the microstructure which develops with the plasticity. This has been carried out with various levels of doping with Se and with Zn (Rabier et al., 1985a). Deformation studies have also been made of $Cd_xHg_{1-x}Te$ (CMT), which is used in the optoelectronic industry for $0.2<x<0.3$ ($E_g \sim 0.2$ eV) and $x \sim 0.7$ ($E_g \sim 0.8$ eV). Uniaxial compression measurements have been conducted on single crystals to determine shear characteristics as a function of x for a range of orientations when a maximum is observed for $x \sim 0.75$. Measurements are being made of the Hall effect, electron beam induced current (EBIC), and deep level transient spectroscopy (DLTS) (Bardot, 1985).

AlN sintered with Y_2O_3 as additive is used in very large scale integrated circuitry (VLSI) applications; it is a high-density substrate with good thermal conduction and is an electrical insulator. During the processing, the garnet $Y_3Al_5O_{12}$ is formed. The microstructure of this material is being studied by TEM to characterize the sintered state (Denanot et al., 1985).

4 SOLID PRECIPITATES

Irradiation of metals and Si by Xe ions results in the formation of solid ppt of Xe, and LMP has recently been studying these ppt extensively (Templier et al., 1985). TEM, electrical resistance, extended x-ray absorption fine structure (EXAFS), Rutherford backscattering (RBS), and x-ray diffraction studies have been carried out over a range of temperatures. In some cases, epitaxial ppt are observed and in other cases amorphous transitions.

Al-Ag, Al-Cu and Al-Zn alloys have been formed by irradiating single-crystal Al foils with the appropriate ion. The formation of Guinier-Preston (GP) zones and ppt have been followed by x-ray diffraction and by TEM. Al_2Cu(θ phase) ppt has been identified and the irradiation dependence of its formation examined (Goudeau et al., 1985).

Other metal systems with solid ppt that have been studied are:

- Internal oxidation of Cu-Al single crystals
- Cu-Al alloys formed by powder metallurgy (patent ANVAR No: 8507157)
- $Cu-Al_2O_3$ mechanical properties (Grosbras et al., 1984b)
- Al-SiC system (Cahoreau and Humphreys, 1984).

5 IMPLANTATION DAMAGE

LMP has carried out ion bombardments of up to 200 keV for the purpose of investigating the formation of new alloys and surface treatments and the study of defects caused by irradiation.

The materials they irradiated are: Si by hydrogen, Al by Al, Fe by Al, and Fe by Co. For the Fe alloys, the magnetic hyperfine structure has been related to composition and irradiation conditions (Fnidiki and Eymery, 1985; Dinhut et al., 1985).

The alloys NiAl and also NiTi transform from a crystalline to an amorphous state under irradiation, and this condition has been studied by CEMS and by TEM (Bodin, 1986; Metari et al., 1986).

Studies were made of damage caused by electron irradiations at 20 K using a Van de Graaff generator. Alloys examined were FeAl, NiAl, and NiTi (Jaouen et al., 1985).

6 ION BEAM MIXING REACTIONS (IBMR)

Ion beam mixing reactions are made by the evaporation (generally onto a neutral substrate) of alternate layers of metals, usually less than 1000 Å thick, to form bilayers or multilayered stacks. These are then ion bombarded, typically by N or Ar ions at 50 to 100 keV. The equipment to carry this out is under development at Poitiers.

Amorphous structures are obtained in some cases while metastable structures are formed in others. These are studied by TEM, RBS, electrical resistance, and CEMS.

The systems examined include: Fe-Al, Ni-Al, Co-Al, Fe-Mg, Cu-Ni, Ni-Ti, and Cu-Ti. FeMg alloys are normally immiscible, but alloys can be formed under conditions of IBMR. Amorphous structures are formed in the case of Ni-Ti (Jaouen et al., 1985).

These surface treatments or coatings are of interest for obtaining improvements in wear resistance, friction, and corrosion behavior as, for example, with TiNi irradiated by N.

Some very interesting experiments in dynamic ion beam mixing are being undertaken by Delafond and coworkers. An implanter has been modified to permit double evaporation to be carried out simultaneously with ionic bombardment to provide a continously controlled composition. This follows their earlier studies, which consisted of depositing bilayers or multilayers and then applying ion beam mixing, repeating as required. The present work concerns depositions of metal carbides on metal substrates.

7 THEORETICAL STUDIES

A wide range of theoretical studies are carried out at Poitiers to model the behavior of defects and their effects on mechanical properties. Some calculations, with references, are:

- Interactions between point defects and dislocations (Rabier et al., 1985b)
- The dislocation core and jogs in ordered B2 alloys (Benhaddane et al., 1984)
- Antiphase boundary energies in $L1_2$ ordered alloys (Veyssiere et al., 1985).

8 SUMMARY

The laboratory of Metal Physics in Poitiers uses TEM, SEM, SIMS-ESCA, CEMS, and ASAXS to examine the very fine microstructure of crystalline solids, usually single crystals; dislocations, subgrain boundaries, ppt, inclusions, GP zones, and composition gradients are studied. The objective is always to determine their relationship to physical properties, particularly deformation mechanisms, surface properties, and radiation damage effects. Theoretical studies are also carried out to characterize the properties of defects in solids.

The materials examined cover a wide range:

- Superalloy structures--Ni_3Al, Ni_3Ge, Ni_3Si
- Alloys--Cu-Al, Fe-Cr-Ni, Ni-Ti
- Metals with ppt--Cu-Al_2O_3; Al-SiC, Xe in Si, Xe in Al
- Semiconductors materials--Si, GaAs, AlN+Y_2O_3, $Cd_xHg_{1-x}Te$

- Alloys by irradation--Al-Ag, Al-Cu, Al-N, Fe-Al, Ni-Al, Ni-Ti
- Ion beam mixing--Ni-Al, Co-Al, Fe-Mg, Cu-Ti

Recent particularly interesting results are (1) composites containing Cu and Al made from powders, having good mechanical and electrical properties; (2) the plastic properties and dislocation structures of high-temperature Ni alloys; (3) the nature of Xe ppt in metals; (4) ion beam mixing of TiN coatings on Al or Ni, improving wear and corrosion resistance; (5) carbides on metal surfaces by dynamic ion beam mixing reactions, permitting thermal expansion matching with the substrate.

LMP's equipment developments have been concerned with the preparation, treatment, and examination of the surface condition of materials following ion implantation, evaporation, CVD at low temperature, and laser beam recrystallization. Many studies are carried out in collaboration with industry and with universities not only throughout France but also in the US.

It is difficult not to be impressed by the work of the Laboratory of Metal Physics in Poitiers.

9 REFERENCES

Bardot, J.F., *Microhardness of CdHgTe Alloys*, (M.S. thesis, Université de Poitiers, 1985).

Benhaddane, K., and P. Beauchamp, "A Computation of (110) Intrinsic Stacking Fault Energies in B2 Alloys," *Physica Status Solidi A*, 86 (1984), 613.

Bodin, D., *Reflexion Mössbauer Spectroscopy of Irradiated* Ni_{50}-Ti_{50} *Alloys*, (Ph.D. thesis, University of Poitiers, 1986).

Cahoreau, M., and F.J. Humphreys, "The Rotation of Particles During the Deformation of a Two-phase Copper Alloy," *Acta Metallurgica*, 32 (1984), 1365.

Denanot, M.F., J. Delafond, and J. Grilhé, "Formation of an AlN Continuous Layer by Nitrogen Ion Implantation in Aluminum Alloys," *Radiation Effects*, 44 (1985).

Dinhut, J.F., P. Bouillaud, and J.P. Riviere, "Irradiation aux Ions d'un Film Mince d'Alliage Fe-65at.percent Co-35 at.percent; Production d'un Verre Métallique $Fe_{50}Co_{30}P_{20}$," *Physica Status Solidi A*, 87 (1985), 199.

Eymery, J.P., P. Moine, and D. Bodin, "Amorphous to Crystal Transition Characterized by CEMS and TEM in ^{57}Fe Implanted Ni-Ti (50-50)," *Journal of Physics* C8-211, suppl (1985), 211.

Fnidiki, A., and J.P. Eymery, "Sur la Transition Ordre-déSordre Creée par Implantation Ionique dans Fe-Co 50 percent at," *Scripta Metallurgica*, 19 (1985), 329.

Goudeau, P., A. Naudon, A. Fontaine, and C.E. Williams, "Diffusion Centrale Anomale sur les Zones de Guinier-Preston dans l'Alliage Aluminium-Zinc," *Journal of Physics Letter*, 46 (1985), 255.

Grihlé, J., F. Tranchant, J. Vergnol, and M.F. Denanot, "Influence de la Nature des Fautes d'Empilement sur la Déformation par Maclage des Solutions Solides C.F.C. Monocristallines," *Revue de Métallurgie* (1985), 1-25.

Grosbras, P., J.L. Demenet, H. Garem, and J.C. Desoyer, "Equilibre Statique entre Dislocations Partielles dans du Silicium Déformé sous Contrainte Uniaxiale," *Physica Status Solida A*, 84 (1984a), 481.

Grosbras, M., M. Cahoreau, E. Dedieu, and M. Zahzouh, "Deformation Plastique à Froid des Monocristaux Composites à Base de Cuivre," *Memoires et Etudes Scientifiques Révue Metallurgie* (1984b), 941.

Jaouen C., J.P. Riviere, A. Bellara, and J. Delafond, "Ion Mixing in Fe-Al, Ni-Al and Co-Al Multilayered Thin Films," *Nuclear Instruments and Methods in Physics Research*, Section B, Vol 7/8 (1985), 591.

Kim, J.J., P. Moine, and D.A. Stevenson, "Crystallization Behaviour of Amorphous Ni-Ti Alloys Prepared by Sputter Deposition," *Scripta Metallurgica*, 20 (1986), 243.

Kubin, L.P., and Y. Estrin, "A Nonlinear Aspect of Crystal Plasticity: The Portevin-Le Chatelier Effect," *Journal of Physics*, 47 (1986), 497.

Lepinoux, J., and L.P. Kubin, "*In situ* T.E.M. Observations of the Cyclic Behaviour in Persistent Slip Bands in Copper Single Crystals," *Philosophical Magazine A*, 51 (1985), 675.

Metari, K., O. Popoola, J.P. Villain, and P. Moine, "Wear Behaviour of N+ Implanted Ni-Ti Alloys," *Scripta Metallurgica*, Vol 20, No. 3 (1986).

Rabier, J., H. Garem, J.L. Demenet, and P. Veyssiere, "Plastic Deformation of GaAs Single Crystals at Room Temperature and the Influence of Doping," *Philosophical Magazine A*, 51 (1985a), 67.

Rabier, J., and M.P. Puls, "Atomistic Model Calculation of Pipe-diffusion Mechanism in MgO," *Philosophical Magazine A*, 52 (1985b), 462.

Templier, C., B. Boubeker, H. Garem, E.L. Mathe, and J.C. Desoyer, "Precipitation of Implanted Xenon in Silicon," *Physica Status Solidi A*, 92 (1985), 511.

Veyssiere, P., J. Douin, and P. Beauchamp, "On the Presence of Superlattice Intrinsic Stacking Faults in Plastically Deformed Ni_3-Al," *Philosophical Magazine*, 51 (1985), 469.